



Trace-level measurement of complex combustion effluents and residues using multidimensional gas chromatography–mass spectrometry (MDGC–MS)

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Abstract

The identification and quantitation of non-method-specific target analytes have greater importance with respect to EPA's current combustion strategy. The risk associated with combustion process emissions must now be characterized. EPA has recently released draft guidance on procedures for the collection of emissions data to support and augment site-specific risk assessments (SSRAs) as part of the hazardous waste incineration permitting process. This guidance includes methodology for quantifying total organic (TO) emissions as a function of compound volatility. The ultimate intent is to compare the amount of organic material identified and quantified by target analyte-specific methodologies to organic emissions quantified by the TO methodology. The greater the amount accounted for by the target analyte-specific methodologies, the less uncertainty may be associated with the SSRAs. A limitation of this approach is that the target analyte-specific methodologies do not routinely quantify compounds of low toxicological interest; nor do they target products of incomplete combustion (PICs). Thus, the analysis can miss both toxic and non-toxic compounds. As a result, it is unknown whether the uncharacterized fraction of the TO emission possesses toxic properties. The hypothesis that we propose to test is that organic emissions and organics extracted from particulate matter (PM) are more complex than standard GC-MS-based instrumentation can currently measure. This complexity can affect quantitation for toxic compounds, thereby potentially affecting risk assessments. There is a pressing need to better characterize these organic emissions from hazardous waste incinerators and PM extracts from various other combustion sources. We will demonstrate that multidimensional gas chromatography–mass spectrometry (MDGC–MS) procedures significantly improve chromatographic separation for complex environmental samples. Sequential repetitive heart-cutting MDGC, with coupled mass spectrometry will be shown to be a complete analysis technique. The ability of this technique to disengage components from complex mixtures taken from hazardous and municipal waste incinerators will be shown. © 2002 Published by Elsevier Science Ltd.

1. Introduction/background

Gas chromatography–mass spectrometry (GC–MS) using open tubular columns (OTC) is a common and versatile technique for measuring all types of organic emissions and extracts from combustion residues. It combines specificity for target analyses with universality for unknowns, and reasonable sensitivity for both. However, with regard to many combustion effluents or extracts, even highly efficient single-gas chromatographic (OTC) systems have a substantial amount of superpositioning of analyte zones. This co-elution seriously restricts the mass spectral analysis of individual

constituents and prohibits accurate quantitation of many of the solutes. With the application of class fractionation techniques, solid-phase extraction procedures, and other sample “clean-up” procedures, such complex samples can be subdivided and simplified. However, the sheer number of compounds in these various fractions (and ever-decreasing detection limits) still requires enhanced analytical separation power, such as that available with the use of multidimensional gas chromatography (MDGC).

The separating power of MDGC has been known for many years. Giddings (1987), Schomberg et al. (1975), Bertsch (1978), Cortes (1990), and Liu and Phillips (1991) have emphasized the power of these MDGC approaches, and there has been much interest over the past decade in attaching hyphenated instrumental techniques

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to such assemblies. Coupling a mass spectrometer to the output channel of an MDGC system has been recognized as essential for qualitative analysis.

MDGC systems and associated hyphenated instrumentation were introduced in the mid-1970s. However, new instrumental developments and advances (in many technologies) have only recently permitted special measurements to be made with complex effluent samples. Modulation procedures pioneered by Liu and Phillips (1991) allowed the possibility of performing separations for extremely complex organic samples to be realized. Many instrumental advances need to be refined before these technologies can be used in routine laboratory procedures. New developments in providing analytical selectivity in both chromatography and spectrometry have been recently introduced. These improvements in analytical capabilities are now being introduced in commercial instrumentation assemblies. With the advent of fast GC and rapid time of flight mass spectrometry, the turnaround time for many analyses shall be reduced in the future.

1.1. Analysis of complex combustion effluent samples

Clearly, effluents from combustion sources can be at least as complex as environmental or petroleum samples. Most combustion systems are capable of destroying the organic feedstocks that come in direct contact with the flame. However, the great majority of compounds observed in combustion effluents, products of incomplete combustion (PICs), may be formed in reactions occurring outside of the flame zone (Dellinger, 1989; Dellinger and Taylor, 1994; Ruby et al., 1997). These reactions can be at low, intermediate, or high temperatures, catalyzed by surfaces, and subjected to a wide range of oxygen concentrations, organic concentrations, mixing, and residence times (Chang et al., 1988; Clark et al., 1988; Cundy et al., 1989). With such a wide range of potential PIC formation conditions and extreme variation in the composition of hazardous waste feedstocks, trace-level, highly complex combustion emissions are possible.

Although considerable effort has been expended on characterization of emissions from some combustion sources, the complexity of the effluent has resulted in the separation of only a small percentage of the number of chemicals emitted (Talyor et al., 1998). And of the chemicals that can be separated, only a small percentage of those can be identified. Further, of those that we can identify, only a small portion is toxic (Taylor et al., 1998). MDGC–MS may be a solution to these problems of sample complexity and coelution.

Although the exact pattern of the chromatogram may vary among combustion sources, the general pattern, complexity, and lack of resolution are similar. This lack of detailed and thorough analysis has prevented a com-

plete assessment of the toxicity of essentially any combustion source. Thus, we have begun experimentation with MDGC–MS to qualitatively identify chemical compounds in emissions samples, as well as to measure accurately the quantitative amount of each chemical compound without interference from other chemical compounds.

Ultimately, the ability to correctly identify and quantify components in a complex mixture may be important and useful in determining the risk and toxicity associated with any combustion source. In addition, determination of the amount of a particular compound is critical to measure, without including peak areas of coeluting non-toxic compounds with the areas of toxic target compounds. Clearly coelution can classify a particular sample as more toxic than it is, or alternatively, less toxic than it is.

The identification and quantitation of non-method-specific target analytes have greater importance with respect to EPA's current combustion strategy. The risk associated with combustion process emissions must now be characterized. EPA has recently released draft guidance on procedures for the collection of emissions data to support site-specific risk assessments (SSRAs) as part of the hazardous waste incineration permitting process (US-EPA, 1998). This guidance includes methodology for quantifying total organic (TO) emissions as a function of compound volatility (Martz et al., 1996). The ultimate intent is to compare the amount of organic material identified and quantified by target analyte-specific methodologies to organic emissions quantified by the TO methodology. The greater the amount accounted for by the target analyte-specific methodologies, the less uncertainty may be associated with the SSRAs. A limitation of this approach is that the target analyte-specific methodologies do not routinely quantify compounds of low toxicological interest. As a result, it is unknown whether the uncharacterized fraction of the TO emission possesses toxic properties. MDGC combined with MS offers an ability to identify and quantify both the toxic and non-toxic composition of TO emissions.

In this contribution, we report our progress in the application of various forms of MDGC–MS to provide information about complex mixtures, which will improve risk assessment estimates. We show examples of shortcomings of single-column GC for some complex mixtures and how these shortcomings can be overcome by MDGC–MS analyses.

The goal of optimizing complex organic mixture analyses is the major goal of MDGC–MS and the size of this development and research endeavor is intense. A large future task is that of simplifying the output data produced by MDGC–MS instrumentation. It is anticipated that with newly designed instrumentation, as many as 40,000 analytes could be addressed within one

particular analysis. Several research areas need to be addressed, such as the removal of chemical interferences, solute overloading with OTCs, the use of deconvolution procedures for advanced MDGC–MS systems, and the improvement of trace analysis capabilities involving GC and MS instrumentation.

1.2. Conventional MDGC: experimental difficulties

Researchers have been reluctant to exploit the many advantages of multidimensional gas chromatography (compared to conventional GC) due to the exacting nature of the instrumentation, flow path connections, challenging pneumatics, pressure and flow adjustments, analysis times, etc. Dual column systems with intermediate cryotrapping all located in the same chromatographic oven (Rubey et al., 1998) may require as many as 10 different ferrule connections made inside the chromatographic oven (Fig. 1). Each of these ferrules must seal without failure in spite of a great deal of thermal cycling of the oven and high inlet pressures necessary for optimal gas velocities through two-column systems. In addition, cryogenic trapping of solute zones has been found to provide better resolution for the multidimensional separation (Rubey et al., 1986; Anderson et al., 1995) in most cases. In many MDGC systems, unless cryotrapping takes place after the first column and additionally, at the beginning of the sec-

ondary column, the resolution gained from the high-resolution primary column separation may be lost. This degree of cryotrapping also emphasizes the potential problems for leaking ferrules, which are routinely subjected to changing temperatures from -60°C or lower to 300°C or higher.

In addition to these formidable problems, the analyses conducted with some of the current forms of MDGC are extremely long. Fig. 2 represents a chromatographic tracing of a complex sample from a MDGC system such as described above, that is, a system with intermediate cryotrapping, heating and retrapping on the secondary column (Striebich et al., 1999). This sample was the semi-volatile fraction of the effluent obtained using a U.S. EPA Modified Method 5 sampling train and had been subjected to liquid extraction and solvent volume reduction. The upper signal tracing shown in Fig. 2 represents the output from the initial OTC (5% phenylmethylsiloxane) in the previously described MDGC–MS system. The lower signal is the output from the second dimension OTC (1701 cyanosiloxane) as detected by the MS. Fig. 2 shows that a 15 s-wide heart cut, which appeared to be a doublet in the initial GC output, is in reality many solutes and, furthermore, they are now sufficiently separated for identification by MS. The 10 s wide singlet also shows many solutes, and it is important to notice the excellent baseline for this second chromatogram.

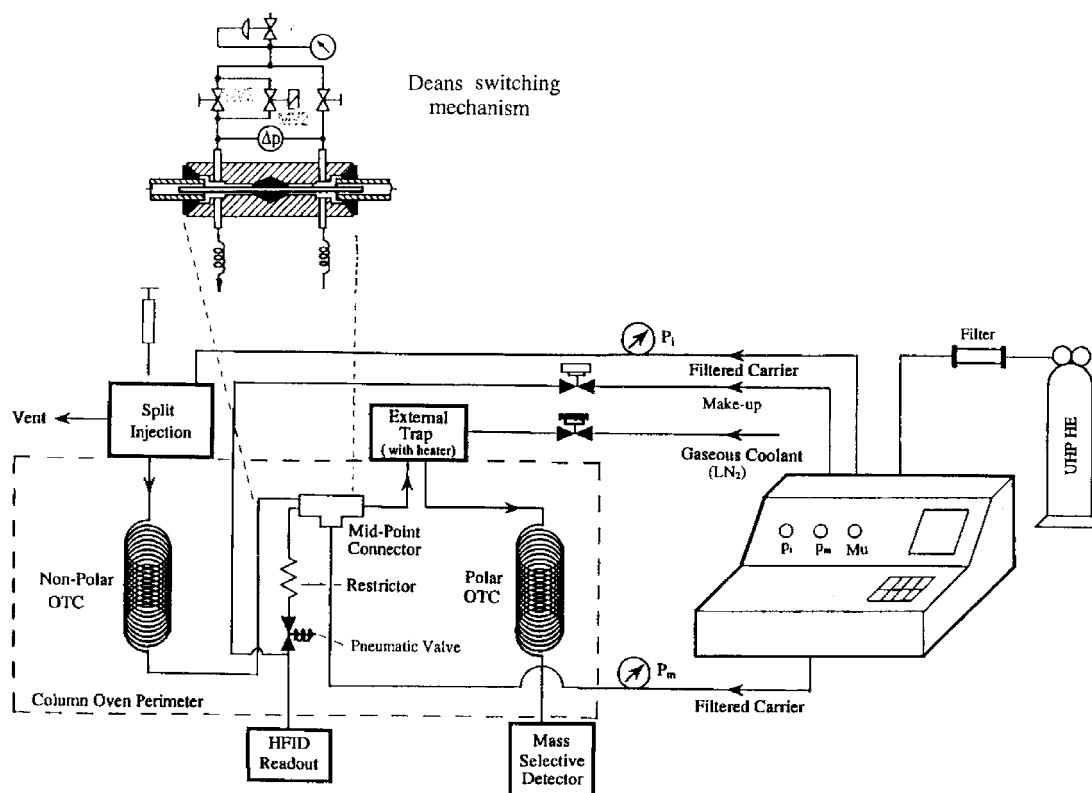


Fig. 1. MDGC system with dual columns and external cryogenic trapping.

Although this sample represented a significant increase in resolving power for the analysis of a complex mixture, the time investment in the separation is, arguably, excessive. After waiting for a cryotrap to cool to trapping temperatures, 40-min primary separation was obtained with a 10-s heartcut directed to the cryotrap. After allowing the primary column temperature program to complete, the oven could be cooled down to sub-ambient temperatures (-60). Then the trap could be heated and the trapped solute compounds released downstream to the secondary column (now cryogenic). The correct inlet pressure could then be obtained and the secondary column programmed temperature run (40 min) could be started. Thus, with waiting times for cooling and heating the traps and columns, it could be possible for each heartcut to be analyzed in 2 h or more. Thus, 10-s of information about the primary chromatogram may have been generated in two hours time, without consideration of spectral interpretation, integration etc. Clearly, increases in *analytical information per unit time* are possible. The clear advantage of this system was that the heating of the external trap never detracted from the width of the injected solute zones because as the trap was being heated, a downstream cryofocussing member (namely, the secondary column) was available to narrow the zone.

Thus, in order to increase the analytical information per unit time, fast GC applications such as microbore gas chromatography on the primary or secondary column could be performed. The related literature on faster MDGC includes a thermal modulation technique (Phillips and Ledford, 1996; Gaines et al., 1998) with

fast secondary column detection. Marriot and co-workers (Marriot and Kinghorn, 1997; Kinghorn and Marriot, 1998) move a cryogenic system along the length of the column (longitudinal modulation) in order to quickly apply heating and cooling. They also point out that the cryogenic zone need not be moved but rather the column can be moved through the cryogenic zone. This work describes the movement of the column rather than the cryogenic zone. It also uses conventional quadrupole MS instrumentation and techniques, not previously used in MDGC work. This work is also different from previously reported work in that secondary column separations are conducted using longer columns and thus, more resolution. Potentially, this technique could provide a complete analysis of any sample such that every compound eluting from the primary column is directed to the secondary column and then to the detector.

2. Experimental

MDGC–MS was performed using a modified Hewlett Packard 5890 A GC/5970B MSD. Effluent from the primary column (0.25 mm ID, 0.25 μ m film thickness, J&W 30 m DB5MS) was split to an FID for primary column monitoring and also split to the secondary column, the front end of which was contained in a cryotrap. The trap operated at approximately -60 °C while heartcutting and was quickly heated to release the solutes from the trap by moving the column out of the cryogenic zone using a computer controlled linear

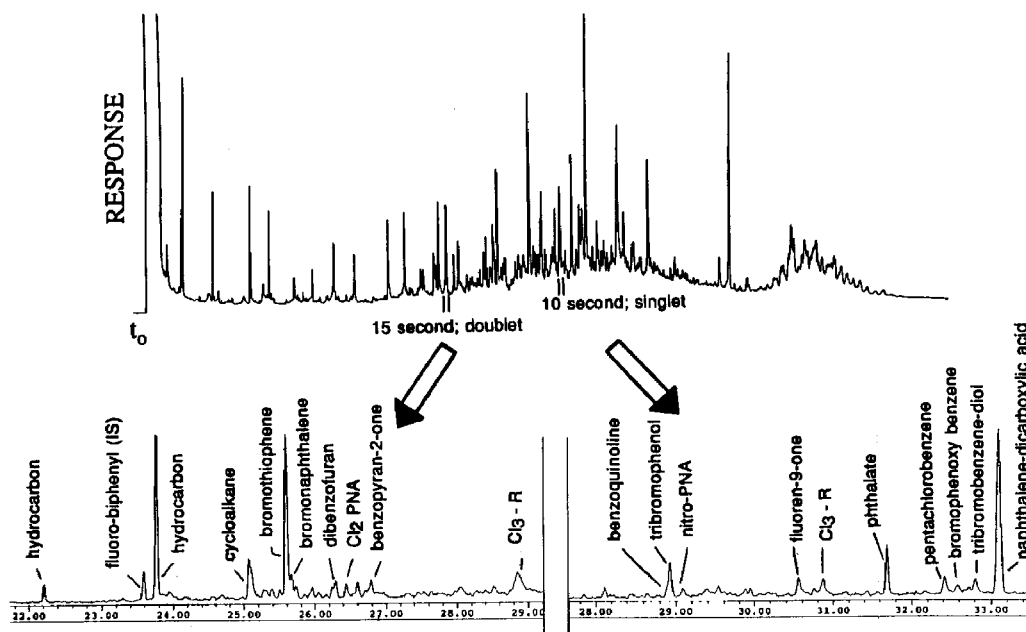


Fig. 2. MDGC–MS analysis of a hazardous waste incinerator effluent sample. The upper signal is from the initial OTC. The lower signal is the MS-output from the second dimension OTC.

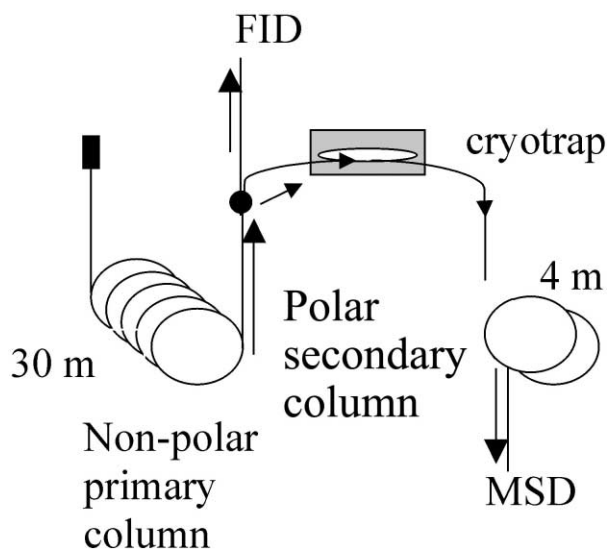


Fig. 3. Simplified schematic of the MDGC-MS with faster secondary column separations.

actuator. The released solute zones migrated through a microbore column (0.10 mm ID, 0.10 μ m film thickness, 4 m Restek RTX 200). Multiple heartcuts were taken during each primary analysis, as had been done on earlier conventional MDGC experiments. The secondary column effluent was directed to the mass selective detector to determine qualitative identifications of products (Fig. 3).

Using this modified MDGC-MS system, the same Modified Method 5 sample from the hazardous waste incinerator (see Fig. 2) was analyzed in demonstrate some of the differences between conventional GC-MS techniques and MDGC-MS.

3. Results and discussion

3.1. Examples of improved separations

Fig. 4 shows a 2 h separation of the hazardous waste incinerator sample on a column similar to that column used in MDGC-MS analysis. In the MDGC analysis, heartcuts were taken from various locations in the chromatogram. An example heartcut is shown in Fig. 5, showing good resolution in the MDGC-MS to separate components even in a wide, 3-min heartcut.

In this particular chromatogram, heartcuts were taken to be 3 min in time and the time for the primary chromatogram was 120 min. These wider heartcuts for longer analyses were taken to simulate narrower heartcuts taken for shorter runs conducted in previous studies (Striebich et al., 1999). Previous heartcuts of 10–20 s for a 30-min primary analysis conducted previously are approximately comparable to this work in which a 3-min heartcut is taken for a 120-min analysis.

Fig. 5 shows an example of two heartcuts taken from 3 min of the 120-min primary separation, focusing the compounds collected and redistributing them to the polar secondary column. The resulting chromatogram shows very good separation between most of the compounds. The compound marked in this chromatogram is an isomer of bromo-dichlorobenzene. Some of the compounds identified in the same heartcut include dibromocyclohexane, naphthalene, dibromobenzene, trichlorobenzene and others.

There are many situations where the secondary separation can do what the primary column cannot do. For example, even in slow (2 $^{\circ}$ C/min) conventional

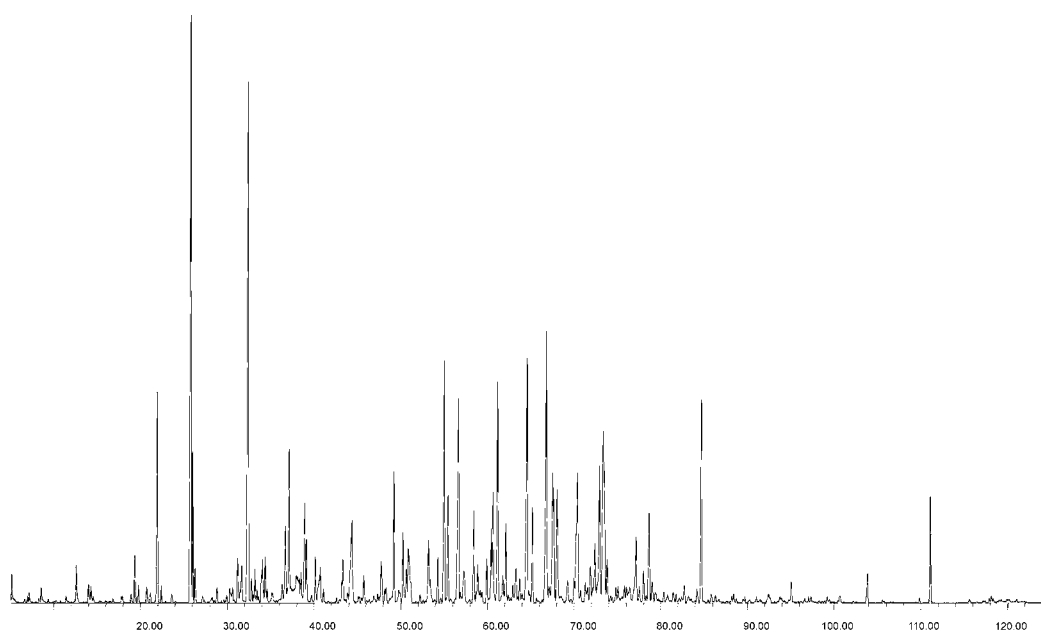


Fig. 4. Conventional, single-column GC-MS chromatogram (> 120 min) of incinerator effluent.

separations, tetrachlorobenzene is not well separated from interferences (Fig. 6). The heartcut corresponding to the MDGC separation of this compound however gives an excellent peak with better results in automated mass spectral interpretation.

Hexachlorobenzene is also shown with minimal resolution by conventional techniques and better resolution by secondary separation (Fig. 7). For MDGC–MS to be

useful, it must be able to provide a better separation than similar single-column separations. Clearly, in some cases, it does a better separation and really shows the potential of the technique to provide more information than can be provided in conventional separations. In other instances, the polar separation may undo the separation of the non-polar column. This shortcoming emphasizes the need to take narrower heartcuts—the

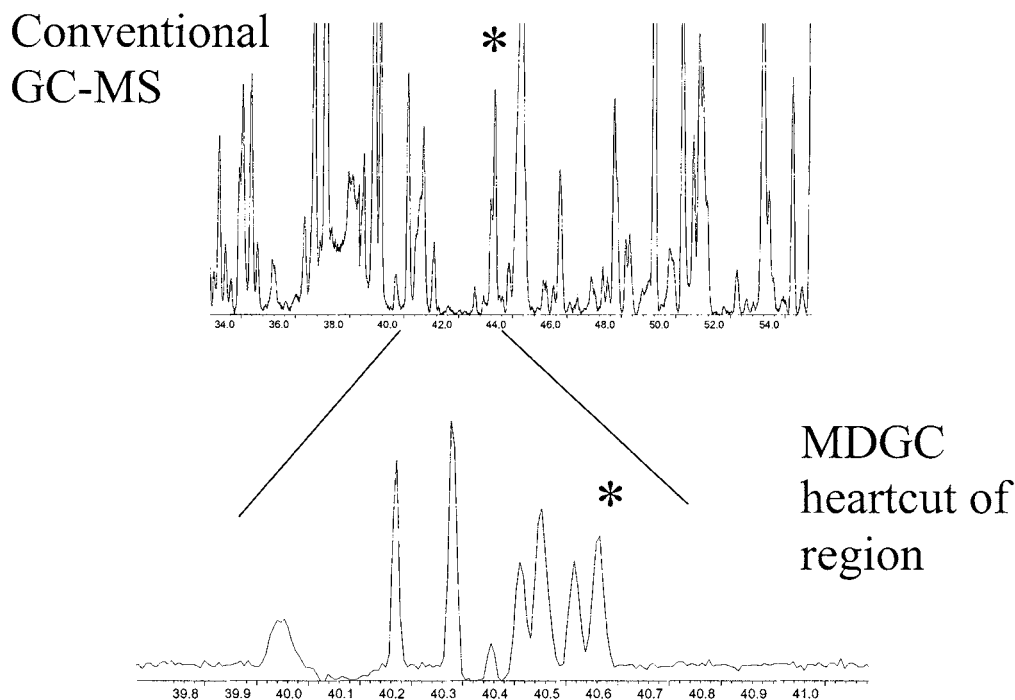


Fig. 5. Example of heartcut shown for the region around bromo-dichlorobenzene.

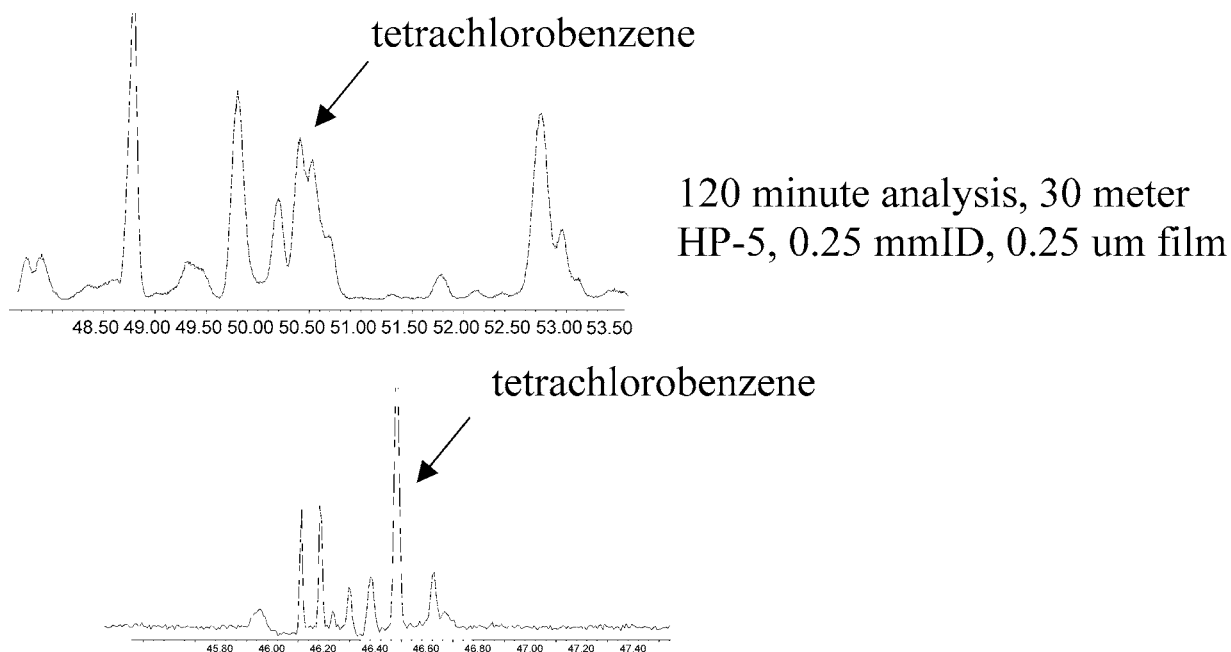


Fig. 6. Separation of tetrachlorobenzene on conventional GC–MS (top) and MDGC–MS (bottom).

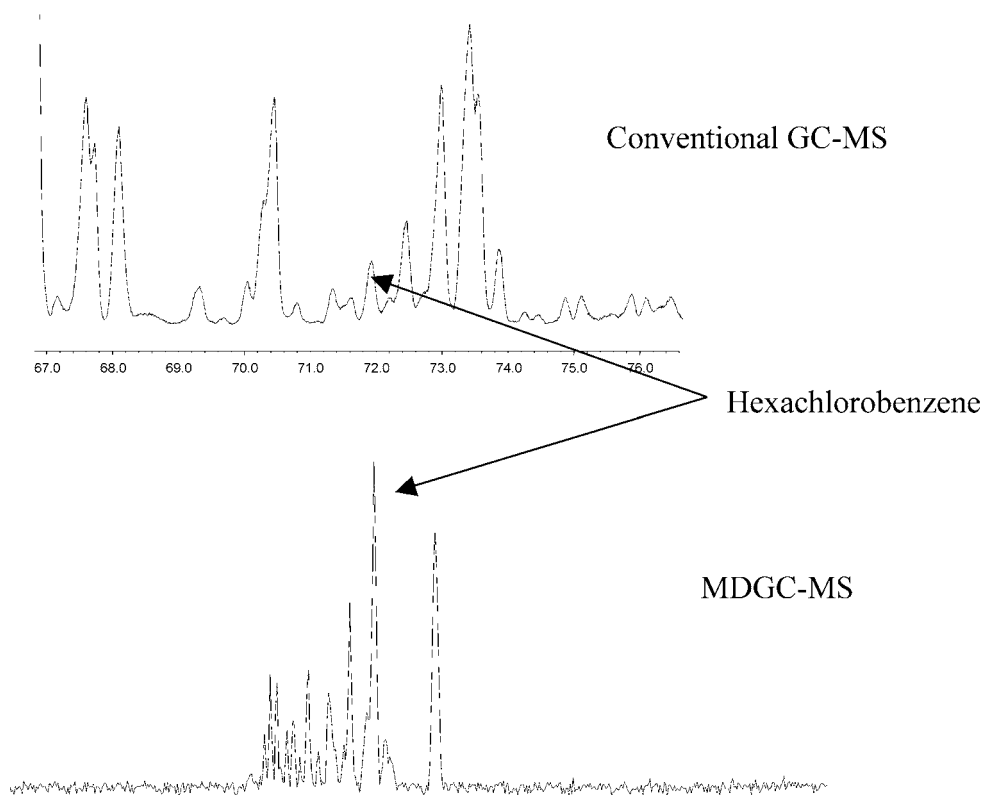


Fig. 7. Improvement in separation of hexachlorobenzene by MDGC.

optimal width being the same as the peak widths from the primary chromatogram.

3.2. Shortcomings of the present system

The MDGC–MS system is continually being modified and improved. The technique of MDGC in general works best if the heartcut times are no longer than the time for one peak width as it elutes from the primary column. In this case, the heartcuts taken were more than 3–5 times that length of time. In spite of efforts to slow the elution of the peaks from the primary chromatogram (by slowing the programming rate and lengthening the run time) the heartcuts were still too wide. Continuing efforts are being made to decrease the size of the heartcuts to be more in line with the width of the eluting solute zone. There is also breakthrough of volatile solutes from the cryotrap. This is almost unavoidable unless the cryotrap is lengthened and/or the temperature of the cryotrap is lowered. Research is being conducted to make this trapping process more efficient for volatile compounds. Since the fused silica column is being moved in and out of a cryogenic region by mechanical means, the column may be subject to breakage, especially considering the possibility of water condensation and freezing around the column. Future designs may incorporate unique heating and cooling techniques without moving parts.

4. Conclusions

MDGC–MS in its various forms has significant potential for obtaining separations of complex mixtures and identifying (through the use of coupled MS) the various separated chemical constituents. This instrumental technique possesses the capability of quantitating separated substances that occur over a wide range of concentrations. Research is continuing in the search for complete analysis of all components of a complex mixture on a multidimensional system. The use of advanced chromatographic techniques and faster, more sensitive detectors would decrease analysis times to where this technique could be used with more confidence and speed. This technique has particular application to the collection of emissions data needed to conduct SSRA as part of the hazardous waste incinerator permitting process. This technique would enable a much more comprehensive characterization of both the toxic and non-toxic PICs present in combustion emissions thereby reducing the uncertainty of the SSRA.

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